

commencing at λ 4736·18, which so far has not been observed in the chromosphere. The other flutings of carbon which are present in the chromosphere do not appear in the coronal spectrum.

The reductions indicate that there may be feeble indications of the presence of some of the chromospheric gases in the inner corona. Thus in photograph 3d, on the north-eastern edge, fragments of rings corresponding to lines of helium at $\lambda\lambda$ 4472, 4714, and 4922 have been recorded; these occur also on the south-western limb, where the chromosphere itself is coming into view, but as the chromosphere was completely eclipsed in the north-east at this stage, the radiations mentioned as occurring there perhaps belong to the inner corona.

A very interesting result of this detailed examination of the photographs is that the chief coronal ring in the green is very closely associated with the form of the inner, and appears to have no distinct connection with the outer, corona. This suggests that the green line of the coronal spectrum is not produced in the outer corona, and that the indications of its presence there on previous occasions, as obtained by slit spectroscopes, were simply due to glare, as in the case of hydrogen and calcium. So far as the photographs taken with the prismatic cameras are concerned, the spectrum of the outer corona gives no indications of bright rings.

The measurements of the coronal rings and the diagram which accompanies this paper have been made by Mr. Fowler.

Dr. Lockyer has investigated the coronal spectrum in relation to carbon, and Mr. Baxandall has made comparisons with the spectra of stars and nebulæ.

"The Ionisation of Dilute Solutions at the Freezing Point." By
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bridge. Communicated by E. H. GRIFFITHS, F.R.S. Received
February 14,—Read February 22, 1900.

(Abstract.)

It is known that the depression of the freezing point of water, produced by dissolving molecularly equivalent amounts of different acids and salts in a given quantity of it, is approximately proportional to the number of ions which these substances must be supposed to yield in order to explain their electrical conductivities. Again, as the concentration of a solution of one such substance is gradually increased, the molecular depression of the freezing point, and the equivalent electrical conductivity, both vary, and vary by amounts which seem in some cases to correspond, but in others to differ considerably.

There appeared reason to suppose that it was desirable to increase

both the extent and the accuracy of our experimental knowledge of these relations. Freezing-point determinations for very dilute solutions are extremely difficult, owing to the minute differences of temperature to be measured, and the results given by various observers showed great discrepancies. On the other hand, the most satisfactory experiments on the electrical ionisation of corresponding solutions had been made at higher temperatures, instead of at the freezing point, at which they should be obtained for purposes of comparison. The fact that the temperature coefficient of conductivity differs for solutions of different concentration, showed that the values of the ionisation would vary if the temperature was changed.

Mr. E. H. Griffiths therefore undertook the examination of the freezing points by the method of platinum thermometry, and the present paper contains an account of corresponding measurements of the electrical conductivities at 0° C.

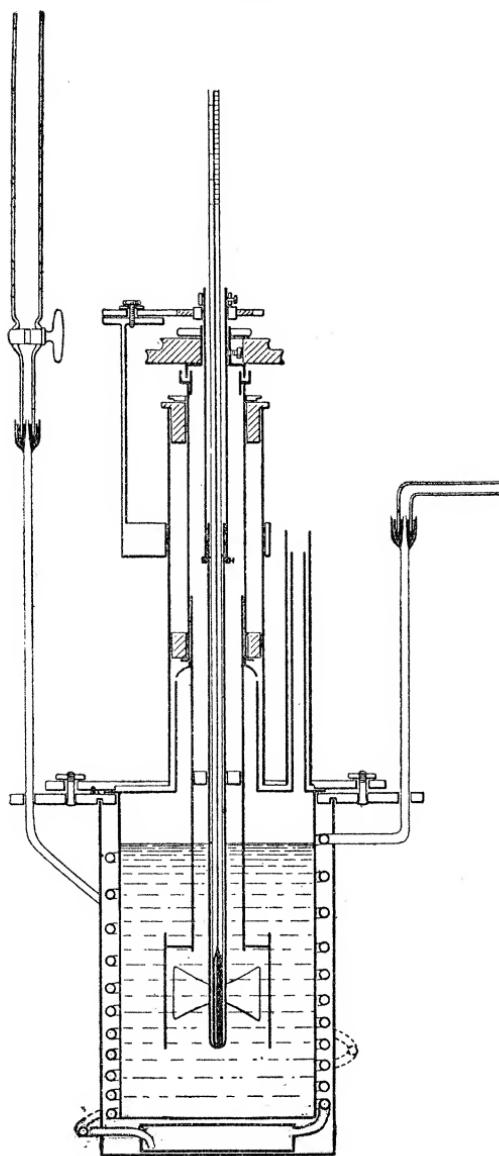
In order to avoid any possible action of glass on the solvent used, it was determined that the water should be obtained from a platinum still and collected in platinum bottles, and that both the freezing point and the electrical measurements should be made in platinum vessels. The structure of the resistance cell is represented in fig. 1. The walls of the vessel itself are used as one electrode, and an insulated platinum cage, suspended inside, forms the other. Within the cage is a platinum screw, mounted on a shaft, which can be turned by means of a hand wheel and cord. This screw is used to insure temperature equality throughout the liquid, and to mix the solutions when made. The shaft of the screw is a hollow tube, closed at the bottom, which contains a thermometer.

Instead of beginning with a strong solution and gradually diluting, it was thought better to begin with a definite quantity of the pure solvent, and, when its resistance had been observed, to add weighed amounts of stock solution of known strength by means of the platinum vessel shown in fig. 2. This vessel will obviously empty itself if a flow of liquid is started by slightly increasing the air pressure at the neck.

In order to obtain a definite quantity of solvent, slightly more than the volume needed was placed in the cell, and the level of the liquid was then adjusted by sucking water through a capillary platinum tube into the glass vessel shown in fig. 3. The bottom of the capillary always comes to the same position relatively to the cell, and, if the sucking pressure is kept constant and equal to that of a water column of about a foot in height, it is found that the amount of water left in the cell is constant to within about one-tenth of a gramme. Thus three independent withdrawals left 219·60, 219·63, and 219·59 grammes. Whenever the cell was dismounted and set up again, this measurement was repeated.

The platinum vessel was surrounded by a brass case, coils of metal

FIG. 1.



tubing being placed in the narrow air space between them. Evaporated ether vapour could be drawn through these coils by an air-pump, and thus the whole vessel cooled. The apparatus was fixed in a large copper tank, which was filled with melting ice.

The electrical resistance measurements were made by the method of alternating currents, but the usual telephone indicator was replaced by a D'Arsonval galvanometer. This was done by using a revolving commutator, which, turned by a hand-wheel and cord, alternated the connections of the bridge with the battery and with the galvanometer simultaneously. The usual Wheatstone-bridge method could then be used, and measurements obtained in the same cell of resistances varying from 10 to 50,000 ohms, the accuracy throughout being at

FIG. 3.

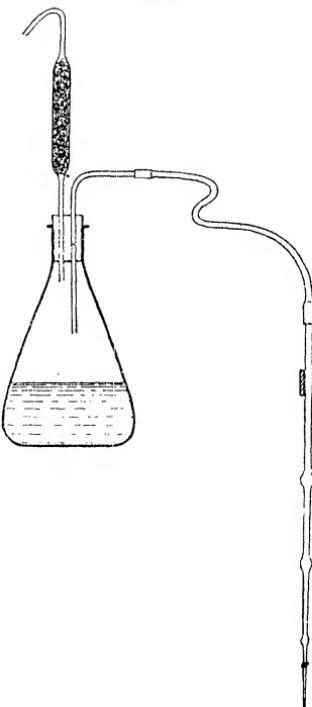
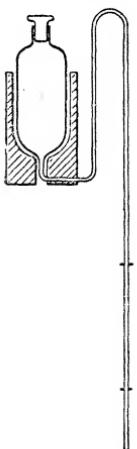


FIG. 2.



least 1 in 1000. The method eliminates several troublesome periodic disturbances, and, in this form, seems entirely satisfactory. The surface of the electrodes was platinised in the usual manner, but was afterwards heated to redness. This process gives a roughened platinum surface of large area, which is less liable to absorb matter from the solution than is the unheated platinum black.

The water used was thrice distilled, twice with alkaline permanganate and once in a platinum still with a trace of acid potassium sulphate. It had an average conductivity at 18° of about 0.9×10^{-15} in C.G.S. units.

Some of the stock solutions for the early part of the work were prepared by Miss D. Marshall, and most of those used in the later measurements were made up at the Cambridge University Chemical Laboratory by Mr. G. Hall, under the advice of Mr. H. J. H. Fenton. Others were prepared by the writer from recrystallised salts obtained from Kahlbaum, of Berlin.

From a knowledge of the weight of solvent used and the weight of stock solution added it was easy to calculate the concentration (m) of the resulting solution in terms of gramme-equivalents of solute per thousand grammes of *solution*. All the experiments were made on solutions so dilute that this way of defining m leads to practically the same results as though the gramme-equivalents of solute were referred to 1000 grammes of *solvent*, or to one litre of solution. The differences only become visible on the curves in the cases of two or three of the strongest solutions of some of the substances used.

The observed resistance is corrected for any slight difference in temperature from zero, and for the increased volume of liquid in the cell due to the volume of stock solution added.

The reciprocal of this corrected resistance is the conductivity in arbitrary cell units, and from this the corresponding arbitrary conductivity of the solvent is subtracted. The resultant conductivity, k , due to the added solute alone, is divided by m , and k/m , the equivalent conductivity, plotted on a diagram as ordinate, the value of $m^{\frac{1}{2}}$, a number proportional to the average nearness of the molecules, being used as abscissa. From these curves the maximum value of k/m is estimated, and taken to represent complete ionisation, the ionisation for the solutions measured being calculated as the ratio between the actual value of k/m and its maximum.

The values obtained for these ionisations were arranged as shown in the following table, which is given as an example, and are plotted as curves on the diagrams appended.

Sulphuric Acid.—Prepared at the Chemical Laboratory by adding the calculated amount of SO_3 to distilled acid. Successive crystallisation brought the melting point of the resultant H_2SO_4 to + 10.5° Cent. The crystals were dissolved in water and the concentration of the solution estimated by the barium sulphate method.

Similar measurements were made on Potassium Chloride, Barium Chloride, Copper Sulphate, Potassium Permanganate, Potassium Ferri-cyanide, and Potassium Bichromate.

In discussing the results, we may first notice that, in cases where it has been possible to obtain values for the ionisation at 18° from Kohlrausch's work, the ionisation curve at 0° is appreciably different from that at 18° , the ionisation falling off more rapidly with increasing concentration at the higher temperature. In the diagrams the values for 0° are given by dots inside circles, and those for 18° by crosses.

In the case of copper sulphate, measurements by the present method were made at 18° as well as at 0° , and are indicated by crosses inside circles; giving a curve which agrees with Kohlrausch's observations at moderate concentrations, but differs from them at extreme dilution.

The normal type of curve is given by potassium chloride, barium chloride, &c. The curve for sulphuric acid departs from this form, as other observers, using glass vessels and working at higher temperatures, have previously found. The drop in this curve at extreme dilution is seen also in solutions of other acids and alkalies, and it has been usual to explain it by supposing that the effective amount of acid is reduced at extreme dilution by interaction with the residual impurities of the solvent. The phenomenon seems too constant for this

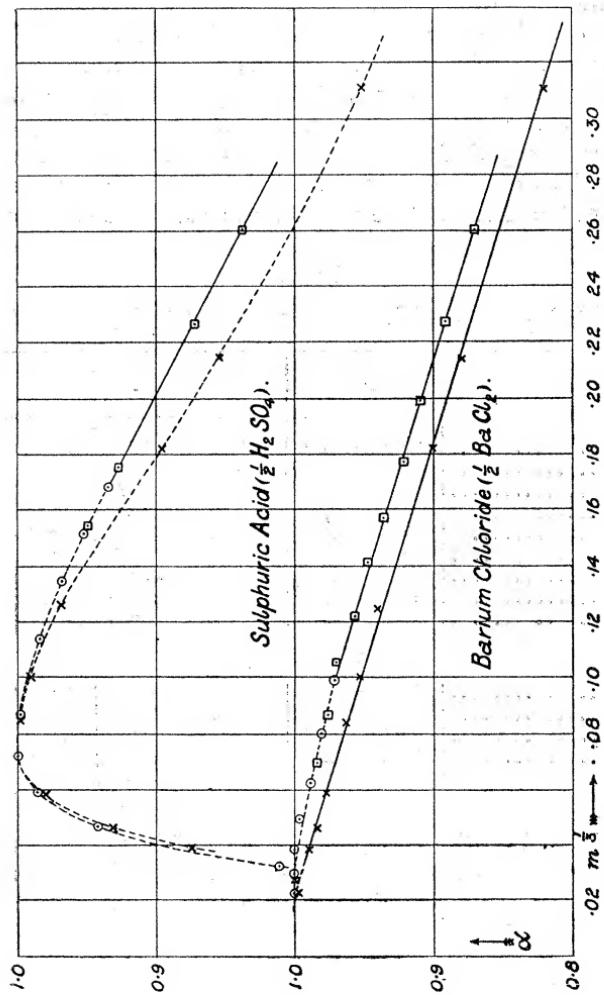
Table I.

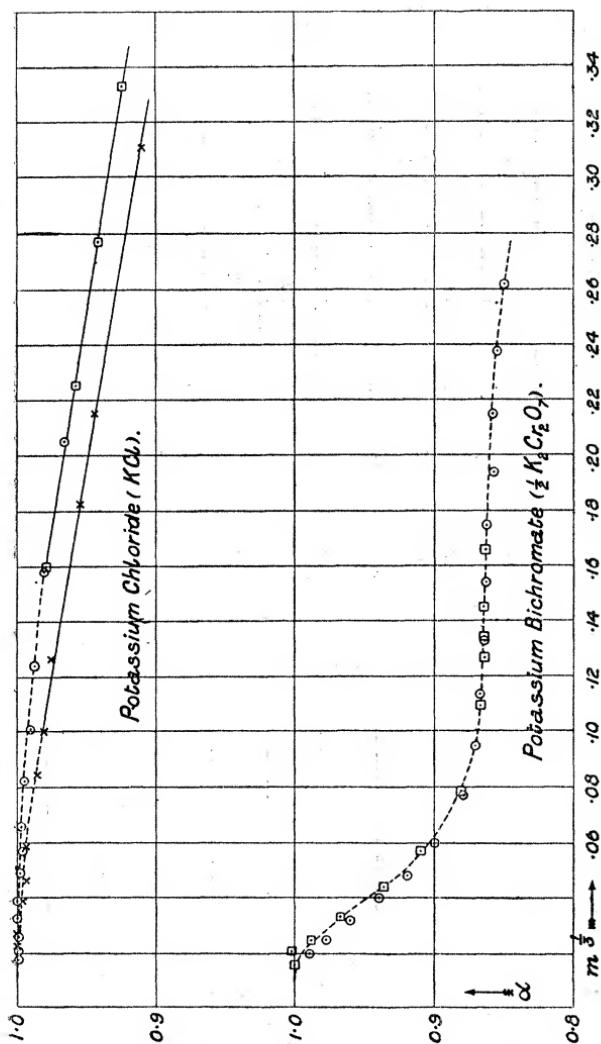
$\frac{1}{2}\text{H}_2\text{SO}_4 = 49.04$, Solvent. Weight = 219.42, R = 40420.

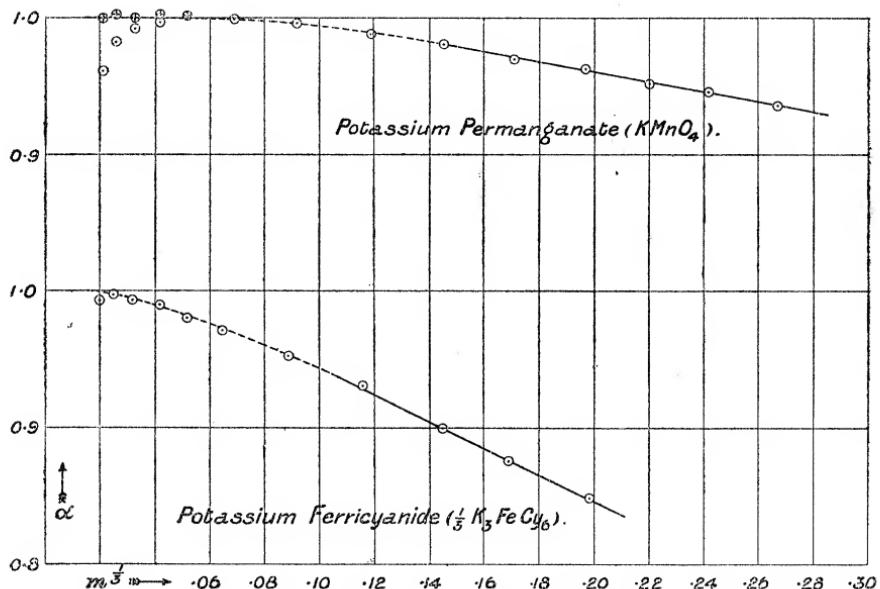
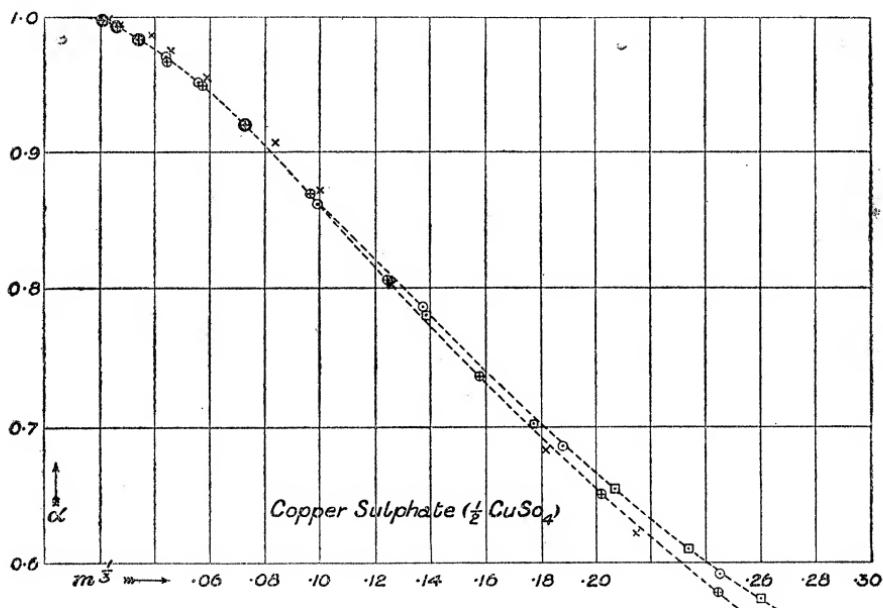
	<i>m.</i>	<i>m³.</i>	<i>R.</i>	<i>K/m.</i>	<i>a.</i>
I	3.254×10^{-5}	0.0319	3106	9.122	0.809
II	9.628	0.0459	954.3	10.62	0.941
III	2.001×10^{-4}	0.0585	444.7	11.10	0.984
IV	3.558	0.0709	247.8	11.26	0.999
V	6.340	0.0859	139	11.26	0.998
VI	1.425×10^{-3}	0.1125	63.11	11.09	0.984
VII	2.411	0.1341	37.75	10.90	0.967
VIII	3.423	0.1507	27.25	10.73	0.951
IX	4.729	0.1678	20.05	10.53	0.934
<i>In Glass Cell.</i>					
I	3.660×10^{-3}	0.1541	1789	0.1552	0.948
II	5.381	0.1752	1246	0.1516	0.926
III	1.158×10^{-2}	0.2262	615.7	0.1426	0.871
IV	1.747	0.2595	424.4	0.1347	0.837

explanation to be satisfactory, and the cause of it may perhaps be connected in some way with the fact that it occurs only in solutions the solute of which gives ions either of hydrogen or hydroxyl, which are ions (1) present in the solvent, (2) possessing greater velocities than any other ions.

The drop in the curve for potassium permanganate is, on the other hand, probably due to interaction between the salt and the solvent impurities. The effect is completed by the first addition of salt, for if a correction be made in the case of the first solution for the salt thus put out of action, it is found that the curve reverts to the normal type. This is clearly shown by the diagram. Again, both in this case and in that of sulphuric acid, it was found that for solutions of great dilution the resistance showed a gradual rise for some time after the







stock solution was added to the solvent, as though the action took time for its completion. While, however, in the case of permanganate this phenomenon was only observed on adding the first lot of stock solution, in the case of acid it appeared in the second solution also. This confirms the idea that the action is not completed by the first addition of acid, though the quantity of acid present must be large compared with the amount of residual impurity in the solvent.

The permanganate measurements also show that the slant of the curve is that of a salt like potassium chloride, with a monovalent acid radicle, rather than that of a salt such as copper sulphate, with a divalent acid. The chemical structure of permanganate in water solution is therefore probably represented by the formula KMnO_4 .

The curve for potassium bichromate appears to consist of two parts, an indication, perhaps, that the ions are different at different concentrations.

In order to collect the results, smoothed values have been obtained from the curves and are appended in Tables IX, X, XI, and XII. The first three tables contain ionisation coefficients at 0° , the concentration being tabulated in different ways. Table XII shows approximate values for the equivalent conductivities at 0° . These were not necessary for the determination of ionisation, so a single value of the cell constant, obtained by comparison of the copper sulphate measurements at 18° with Kohlrausch's absolute values, was used, except for the potassium chloride solutions, which were reduced by a figure given by Kohlrausch for this salt at 0° . The errors will be small, for the amount of solvent left in the cell in each case was very nearly constant, and this is a measure of the accuracy with which the cell is readjusted after being taken to pieces. The results, however, are not supposed to be as trustworthy as those of the ionisation coefficients.

Table IX.—Ionisation Co-efficients at 0°.

m = number of gramme-equivalents of solute per thousand grammes of solution.

<i>m.</i>	KCl.	$\frac{1}{2}$ BaCl ₂ .	$\frac{1}{2}$ H ₂ SO ₄ .	$\frac{1}{3}$ CuSO ₄ .	KMnO ₄ .	$\frac{1}{3}$ K ₃ FeC ₆ .	$\frac{1}{3}$ K ₂ Cr ₂ O ₇ .
0·00001	1·000	1·000	..	0·998	1·000	0·998	0·991
0·00002	1·000	1·000	..	0·993	1·000	0·996	0·980
0·00005	1·000	0·998	0·880	0·981	1·000	0·991	0·952
0·0001	0·999	0·995	0·944	0·967	1·000	0·985	0·929
0·0002	0·998	0·990	0·984	0·947	0·999	0·977	0·902
0·0005	0·996	0·980	1·000	0·908	0·998	0·961	0·880
0·001	0·992	0·969	0·992	0·863	0·993	0·944	0·870
0·002	0·987	0·953	0·974	0·807	0·986	0·919	0·864
0·005	0·976	0·925	0·931	0·717	0·971	0·876	0·863
0·01	0·962	0·896	0·883	0·638	0·955	0·834	0·858
0·015	0·952	0·876	0·851	0·591	0·944	0·853	..
0·02	0·944	0·860	0·825	0·557	0·934	0·847	..
0·03	0·932	0·833	0·784	0·509

Table X.—Ionisation Co-efficients at 0°.

m = number of gramme-equivalents of solute per thousand grammes of solution.

<i>m.</i>	KCl.	$\frac{1}{2}$ BaCl ₂ .	$\frac{1}{2}$ H ₂ SO ₄ .	$\frac{1}{3}$ CuSO ₄ .	KMnO ₄ .	$\frac{1}{3}$ K ₃ FeC ₆ .	$\frac{1}{3}$ K ₂ Cr ₂ O ₇ .
$\frac{1}{3}\frac{1}{2}\frac{7}{12}$	1·000	1·000	..	0·999	1·000	0·999	0·994
$\frac{1}{3}\frac{1}{2}\frac{3}{8}$	1·000	1·000	..	0·996	1·000	0·997	0·985
$\frac{1}{3}\frac{1}{2}\frac{1}{8}$	1·000	0·999	0·795	0·988	1·000	0·994	0·969
$\frac{1}{3}\frac{1}{2}\frac{1}{4}$	1·000	0·997	0·901	0·978	1·000	0·990	0·947
$\frac{1}{3}\frac{1}{2}\frac{1}{2}$	0·999	0·994	0·958	0·963	1·000	0·983	0·921
$\frac{1}{3}\frac{1}{2}\frac{1}{8}$	0·998	0·988	0·991	0·940	0·998	0·974	0·895
$\frac{1}{3}\frac{1}{2}\frac{1}{16}$	0·995	0·980	1·000	0·909	0·996	0·962	0·880
$\frac{1}{3}\frac{1}{2}\frac{1}{32}$	0·992	0·969	0·992	0·865	0·993	0·944	0·870
$\frac{1}{3}\frac{1}{2}\frac{1}{64}$	0·988	0·954	0·974	0·809	0·987	0·920	0·865
$\frac{1}{3}\frac{1}{2}\frac{1}{128}$	0·979	0·934	0·944	0·743	0·977	0·889	0·863
$\frac{1}{3}\frac{1}{2}\frac{1}{256}$	0·968	0·908	0·901	0·666	0·966	0·942	0·861
$\frac{1}{3}\frac{1}{2}\frac{1}{512}$	0·951	0·875	0·847	0·587	0·942	0·852	0·852
$\frac{1}{3}\frac{1}{2}\frac{1}{1024}$	0·930	0·831	0·779

Table XI.—Ionisation Co-efficients at 0°.

n = number of grammé-molecules of solvent per grammé-molecule of solute.

$n.$	KCl.	$\frac{1}{2}\text{BaCl}_2$.	$\frac{1}{2}\text{H}_2\text{SO}_4$.	$\frac{1}{2}\text{CuSO}_4$.	KMnO ₄ .	$\frac{1}{3}\text{K}_3\text{FeCy}_6$.	$\frac{1}{2}\text{K}_2\text{Cr}_2\text{O}_7$.
20000000	..	1.000	..	0.997	..	0.998	..
10000000	..	1.000	..	0.992	1.000	0.997	0.990
5000000	1.000	0.998	0.894	0.979	1.000	0.994	0.976
2000000	1.000	0.994	0.950	0.965	1.000	0.987	0.949
1000000	1.000	0.989	0.989	0.944	1.000	0.979	0.925
500000	0.999	0.989	0.989	0.902	0.999	0.969	0.901
200000	0.997	0.979	1.000	..	0.949	0.878	..
100000	0.994	0.966	0.989	0.856	0.997	0.926	0.870
50000	0.992	0.950	0.970	0.797	0.993	0.897	0.866
20000	0.984	0.922	0.924	0.705	0.982	0.846	0.862
10000	0.974	0.893	0.875	0.626	0.969	..	0.858
5000	0.960	0.857	0.814	0.545	0.952	..	0.846
2000	0.935	0.923

 Table XII.—Approximate Equivalent Conductivities at 0°, in C.G.S. units $\times 10^{13}$.

m = number of grammé-equivalents of solute per thousand grammes of solution.

$m.$	KCl.	$\frac{1}{2}\text{BaCl}_2$.	$\frac{1}{2}\text{H}_2\text{SO}_4$.	$\frac{1}{2}\text{CuSO}_4$.	KMnO ₄ .	$\frac{1}{3}\text{K}_3\text{FeCy}_6$.	$\frac{1}{2}\text{K}_2\text{Cr}_2\text{O}_7$.
0.00001	807	765	..	704	756	964	833
0.00002	807	764	..	701	756	962	823
0.00005	807	763	2309	692	756	957	800
0.0001	806	761	2477	682	756	951	780
0.0002	805	757	2582	668	755	943	758
0.0005	804	750	2624	641	755	928	739
0.001	800	741	2603	609	751	911	731
0.002	796	729	2556	569	746	887	726
0.005	787	708	2443	506	735	846	725
0.01	776	685	2317	450	722	805	721
0.015	768	671	2233	417	714	..	716
0.02	761	658	2165	393	706	..	711
0.03	752	638	2057	359

FIG. 1.

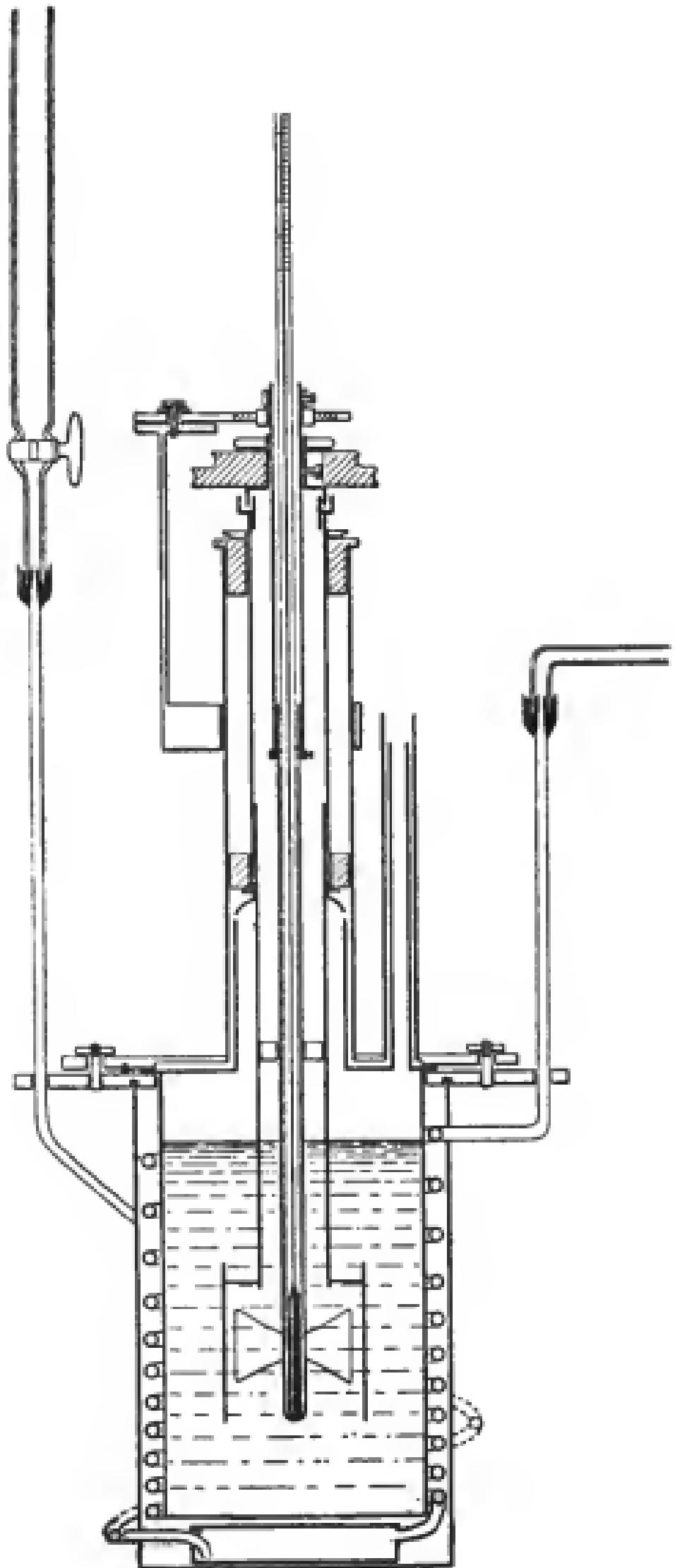


Fig. 3.

